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Simple synthetic access to [Au(IBiox)Cl] complexes†

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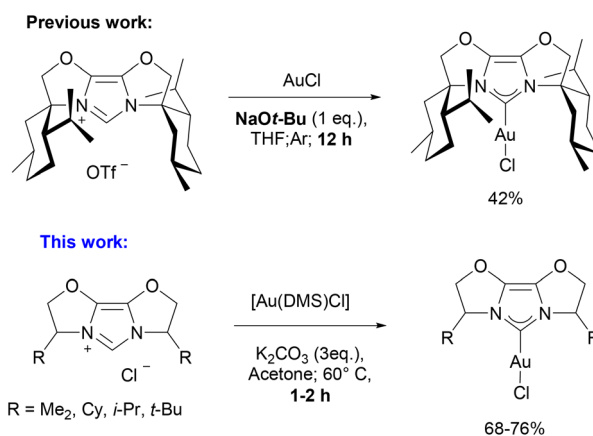
Green and sustainable access to chiral and achiral gold-IBiox complexes is reported. The gold complexes were synthesized using a simple, air-tolerant, weak base protocol carried out in a green solvent. Their catalytic activity was examined in the hydroamination of alkynes. The steric protection afforded the gold center by these ligands was quantified using the % V_{bur} model and compared with the most commonly encountered NHCs.

Introduction

The vast potential of N-heterocyclic carbenes (NHCs) as ancillary ligands in transition metal catalysis has been demonstrated and thoroughly explored during the last two decades.^{1–3} However, some families of NHC ligands, specifically the IBiox series, first reported by Glorius,^{4–7} have been much less explored when compared to the extensive work performed with classical N-heterocyclic carbenes, such as IPr (IPr = [1,3-bis(diisopropylphenyl)imidazolyl-2-ylidene]).⁸ The reason behind this less frequent use is surely associated with the multistep synthetic sequence required to achieve their assembly. Consequently, only a limited number of reports have dealt with the synthesis of IBiox metal complexes.^{4,7,9–14} For instance [Pd(IBiox)Cl₂]₂ complexes were synthesized using IBiox-HOTf salts, Pd(OAc)₂ and LiCl, in THF at 100 °C for 16 h.^{4,9} Another complex, [Pd(IBioxⁱPr)₂I₂], one where two IBiox ligands are bound to the metal was obtained using the IBiox triflate salt and Pd(OAc)₂, with KO^tBu as base in THF as solvent.⁷ [Pd(IBiox)(π -allyl)Cl] complexes have also been synthesized using a strong base, NaO^tBu, in dimethoxyethane (DME).¹⁰ There are also several examples of various rhodium complexes such as [Rh(IBiox)(COE)Cl]₂ which were obtained

via the free carbene route in pentane from [Rh(COE)₂Cl]₂.¹¹ In addition, complexes with the general formula [Rh(IBiox)(L)Cl] (L = COE, NBD, COD) are also reported again via free carbene route with the use of strong bases (KO^tBu) in benzene.^{11,12} Other examples of [M(IBiox)(CO)₂Cl] (M = Rh, Ir) complexes can be found in the literature, synthesized via the transmetalation pathway from [Ag(IBiox)Br] in the case of rhodium,¹³ and via the free carbene route for the Ir complex.⁴ To the best of our knowledge, there is only one example of gold-IBiox complex, which was synthesized from IBiox-HOTf salt with AuCl in the presence of NaO^tBu in THF under inert atmosphere. The desired complex was obtained in a very low yield (42%) (Scheme 1).¹⁴

In spite of the difficult access to this family of NHCs, metal complexes (predominantly with palladium and rhodium) of IBiox ligands have found multiple uses in catalysis.^{4,9,11,14–16}



Scheme 1 Comparison of a previously reported synthetic procedures to [Au(IBiox)Cl] complexes with the “weak base” route.

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Despite the fact that these compounds are of great interest, synthetic routes towards them are quite complicated and usually involve strong bases, toxic solvents and require manipulations under an inert atmosphere.

Therefore, the development of a more user-friendly and efficient synthetic pathway towards M-IBiox complexes would be highly desirable to help democratise their use in catalysis.

Results and discussion

Synthesis of [Au(IBiox)Cl] complexes

Since 2013, when Nolan¹⁷ and Gimeno¹⁸ independently reported simple and efficient approaches to Au-NHC complexes using weak bases, this “weak base route”^{19,20} has been extended to numerous metal-NHC syntheses.^{21–25} We now extend the range of NHC ligands compatible with this weak base route to the IBiox ligand family with a focus on Au-IBiox complexes (Scheme 1). The classical synthetic route employed to access IBiox ligands usually leads to the isolation of triflate IBiox salts.^{4–7} Therefore, our initial attempts to synthesize Au-IBiox complexes using the weak base route made direct use of these IBiox-HOTf salts. Unfortunately, no reaction was observed in this instance when a weak base was used. The concerted mechanism involving the weak base easily rationalises this failure as the nature of the counterion is crucial in dictating the feasibility of product formation. The approach works best with halides as counterion.¹⁹ We next converted the triflate IBiox salts to their chloride congeners (IBiox-HCl) as illustrated in Scheme 2. In the present series, we have targeted for synthesis and further metalation, two chiral (IBioxⁱPr, IBiox^tBu) and two achiral (IBioxMe₄, IBiox6) NHCs. In all cases, the desired IBiox-HCl salts were easily isolated in high yields in microcrystalline forms (Scheme 2).

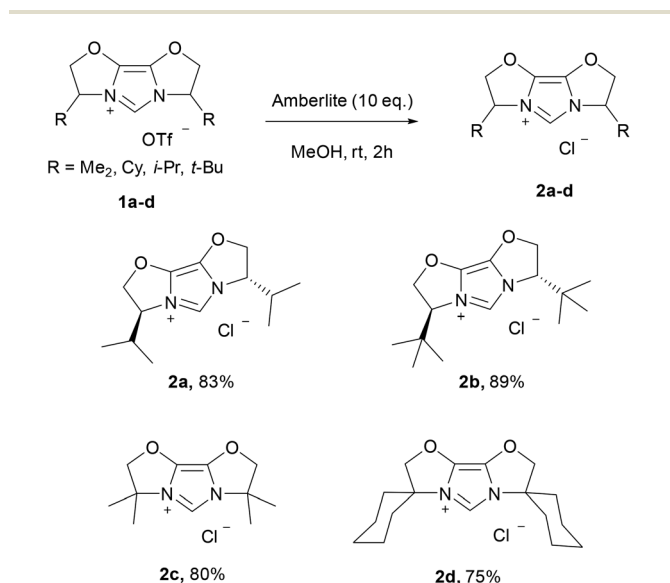
Having **2a–d** in hand, we next turned our attention to the metalation (auration) using our weak base route. Gratifyingly, gold complexes bearing IBiox ligands were synthesized in high yields under much greener reaction conditions, namely by using green acetone as solvent at 60 °C with potassium carbonate as the base (Scheme 3). Reaction times of only one hour were needed to achieve full conversion of IBioxMe₄ and IBiox6 salts to the desired Au-IBiox complexes. Slightly longer reaction times of 1.5 and 2 hours were needed for IBioxⁱPr and IBiox^tBu salts respectively.

To the best of our knowledge, a reported reaction time of 12 hours was needed to reach full conversion for [Au(IBiox[(-)-menthyl]Cl)] complex.¹⁴ Au-IBiox complexes **3a–d** were successfully isolated and fully characterized following this simple protocol and a facile workup (see ESI†).

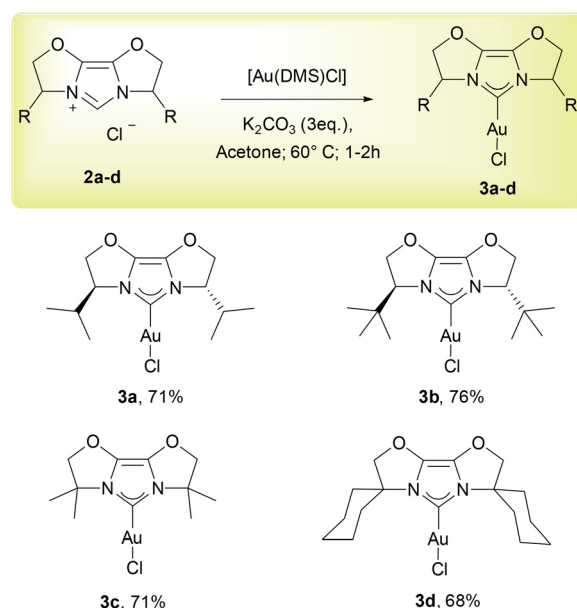
The molecular structures of the obtained gold complexes (**3a–d**) were unambiguously determined by diffraction studies on single crystals (Fig. 1). Crystals suitable for X-ray diffraction were grown by slow vapour diffusion of pentane into saturated CH₂Cl₂ solutions of the complexes.

Selected structural data for these compounds are presented in Table 1. Due to various conformation of cyclohexane rings, two non-equivalent molecules in the crystal unit cell were observed for **3d**. Overall, metrical parameters, (bond lengths and angles) for the synthesized series of IBiox complexes are very similar. Minor deviations from linear geometry are observed in all complexes. The longest Au–C_{NHC} bond is observed for complex **3b**.

Interestingly, when compared with the classical [Au(IPr)Cl] complex, the Au–C_{NHC} bond length in [Au(IPr)Cl] is significantly shorter (1.942(3) Å) than those reported here.²⁶ However, the same bonds in [Au(IMes)Cl], [Au(*It*-Bu)Cl] and [Au(ICy)Cl] are longer than in the IBiox complexes.²⁶



Scheme 2 Synthesis of IBiox-HCl salts.



Scheme 3 Synthesis of gold-IBiox complexes via weak base route.



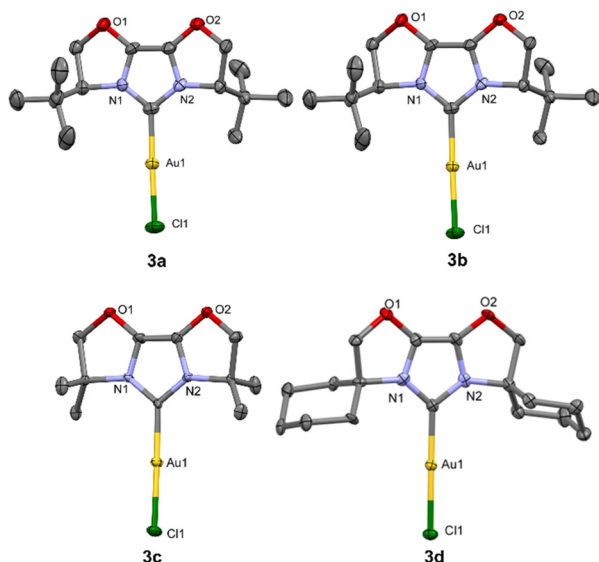


Fig. 1 X-ray molecular structures of complexes **3a–d** are presented (2238228–2238230, 2253267†) showing thermal displacement ellipsoids at the 30% probability level (**3a**) and at the 60% probability level (**3b–d**), hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for each complex

Complex	C _{NHC} –Au	Au–Cl	C _{NHC} –Au–Cl
3a	1.970(7)	2.2833(19)	179.0(2)
3b	1.985(5)	2.2831(15)	178.16(16)
3c	1.979(9)	2.284(2)	178.7(3)
3d^a	1.97(2)	2.276(5)	178.1(6)

^a Metrical parameters are the average values for two independent molecules found in the unit cell.

Complexes **3b** and **3c** have similar Au–C_{NHC} bond lengths as [Au(SIPr)Cl], [Au(SIMes)Cl], [Au(IMe)Cl] and [Au(IAd)Cl]. Au–C_{NHC} bond lengths in complexes **3a** and **3d** are shorter than in the reported classical NHCs with the exception of [Au(IPr)Cl].²⁶ The Au–Cl bond lengths in **3d** are similar to the ones found in [Au(SIMes)Cl], [Au(IMes)Cl], [Au(SIPr)Cl], [Au(IPrMe)Cl] and [Au(IAd)Cl]. The Au–Cl bond lengths in [Au(IBiox)Cl] complexes **3a–3c** are similar to the ones found in [Au(ICy)Cl] and [Au(IMe)Cl].²⁶

Percent buried volume (%V_{bur}) of [Au(IBiox)Cl] complexes

To understand the origin of these variations, we next focused on evaluating the steric pressure (or protection) afforded by the IBiox ligands to the gold center. To permit such an analysis, the percent buried volume^{27,28} (%V_{bur}), a steric descriptor initially conceived to address the non-cone angle depiction of NHC ligands, was used. The large database available for [Au(NHC)Cl] molecular structures make these a convenient scaffold for comparison with other NHC ligand classes.²⁹ Although percent buried volumes of IBiox ligands have already been reported for [PdL(π-allyl)Cl] compounds, these were

determined from DFT-optimized geometries instead of X-ray structures.¹⁰ To the best of our knowledge, there is only one gold-IBiox complex described in the literature, namely [Au(IBiox[(–)-menthyl]Cl)], for which a %V_{bur} value was calculated from X-ray molecular structural data.^{14,30} Therefore, we next calculated %V_{bur} values for the presented IBiox ligands in [Au(IBiox)Cl] complexes in order to compare them with previously reported NHC %V_{bur} values (Fig. 2).^{29,30}

The steric maps and %V_{bur} for [Au(IBiox)Cl] complexes were computed both from X-ray molecular structural data and DFT-optimized geometries (Fig. S1, ESI†) using the SambVca 2.1 developed by Cavallo group.³¹ Despite small variation of %V_{bur} between X-ray and DFT-optimized structures, among the studied IBiox ligands IBiox^tBu (**3b**) has the largest %V_{bur} value (35.3), which is still significantly small compared with the previously reported [Au(IBiox[(–)-menthyl]Cl)] (47.7).³⁰

IBiox^tPr (**3a**) has the smallest %V_{bur} value among the NHCs examined in the [Au(IBiox)Cl] series. Notably, all ligands under investigation display two more occupied and two less occupied quadrants (Fig. 2). Percent buried volumes of the IBiox ligands in gold complexes (**3a–3d**) are smaller compared with commonly used NHCs such as IPr (44.5), SIPr (47.0), SIMes (36.9), IMes (36.5) and IAd (39.8).^{29,30} However, values of %V_{bur} for (**3a–3d**) are larger than ICy (27.4) ligand.^{26,29,32}

Hydroamination of phenylacetylene

We next turned our attention to potential uses of these Au-IBiox complexes in catalysis. During the last decade a vast number of gold catalysts, bearing both phosphines and NHC ligands, have successfully been deployed as catalysts in the hydroamination of C–C unsaturated bearing compounds.^{33–36} We, therefore, thought this a good model reaction to further examine the steric influence of the IBiox architecture but this

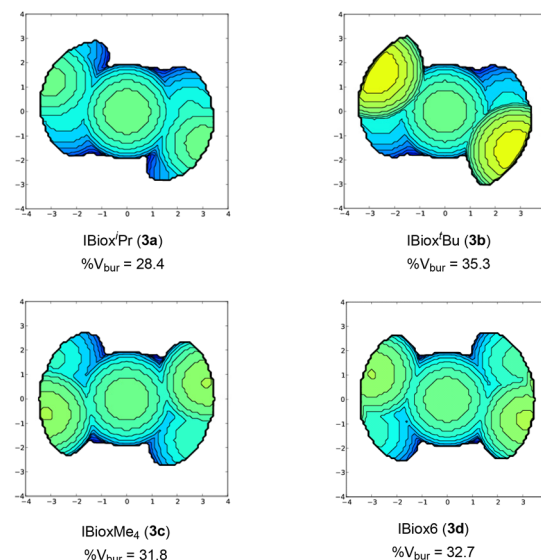
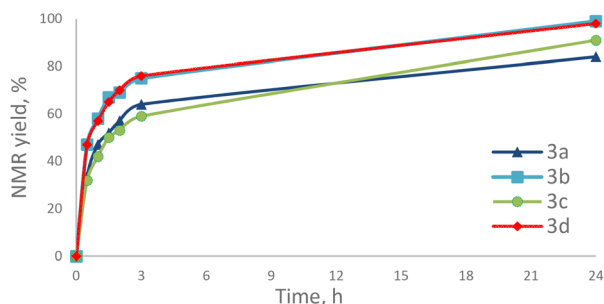


Fig. 2 Steric maps and buried volumes of IBiox ligands in [Au(IBiox)Cl] complexes: NHC structures were extracted from crystal structures ($r = 3.5 \text{ \AA}$, $d = 2.0 \text{ \AA}$, Bondi radii scaled by 1.17) to perform the calculations.



time taking as an observable catalytic reactivity of the Au-IBiox complexes in the hydroamination of phenylacetylene. Our initial screening makes use of the reaction conditions developed by the Gessner group³⁶ for this reaction, namely the use of aniline (1 eq.), phenylacetylene (1 eq.), LAuCl:NaBAR^F = 1:1, 50 °C, in the absence of solvent (neat) (Table 2). Reactions reached full conversion when complexes **3b** and **3d**, bearing the bulkiest ligands, were used as pre-catalysts. In the case of [Au(IBiox^tPr)Cl], the lowest NMR yield was observed (84%) and this after a reaction time of 24 hours.



Notably, all tested [Au(IBiox)Cl] complexes displayed better performance than the conversions obtained with phosphine ligated [Au(L)Cl] complexes, where L = Y_{Ph}PCy₂, Y_{POMe}PCy₂, Y_{PCF₃}PCy₂, PPh₃.³⁶ For all the phosphine-bearing catalysts full conversion was not reached after 24 hours. The best results were observed in the case of [Au(PPh₃)Cl] and [Au(Y_{POMe}PCy₂)Cl], 39% and 42% NMR yields respectively, after 24 h. However, [Au(^{Cy}JohnPhos)Cl] together with [Au(Y_{oTol}PCy₂)Cl] and [Au(Y_{Mes}PCy₂)Cl] showed higher activity than the Au-IBiox complexes: 95%, 93% and 92% NMR yields were obtained after 2 hours. Nevertheless, initial rates of reaction for **3b** and **3d** are faster than for [Au(IPr)Cl] – one of the most commonly used gold catalyst. A 93% NMR yield was observed after 24 h with the latter.³⁶

Table 2 [Au(IBiox)Cl] complexes in hydroamination of phenylacetylene

Time (h)/catalysts	NMR yield (%)			
	3a	3b	3c	3d
0.5	34	47	32	47
1	47	58	42	57
1.5	52	67	52	65
2	57	69	53	70
3	64	75	59	76
24	84	99	91	98

Conclusions

In summary, we have synthesized gold complexes, bearing various chiral and achiral IBiox ligands *via* a simple and sustainable synthetic route. The molecular structures of **3a–d** complexes were determined by X-ray diffraction. The obtained structural data were compared with previously reported NHC–Au congeners. Percent buried volumes for the Au-IBiox complexes **3a–d** were calculated for the first time from XRD data and compared with the other reported IBiox ligand and with commonly used NHCs. IBiox^tBu proves the bulkiest ligand among the studies series. Moreover, catalytic activity of the obtained gold–NHC complexes was examined in the hydroamination of phenylacetylene. Complexes **3b** and **3d** with the bulkiest ligands showed better results than the other IBiox congeners. It is worth noting that all tested complexes proved more active in the examined reaction than previously reported complexes with ylide-functionalized phosphines or PPh₃ as ancillary ligand. Implementation of the described synthetic method to other transition metals and further exploration of properties of the IBiox family are ongoing in our laboratories.

Experimental

General information

All reactions were carried out in air, unless otherwise noted. Solvents and all other reagents were purchased and used as received without further purification unless otherwise stated. All IBiox–HOTf salts were synthesized according to known procedures.^{4–7} Unless otherwise noted, HPLC grade methanol, reagent grade acetone, DCM, pentane, Et₂O and freshly crushed, anhydrous K₂CO₃ were used. Amberlite IRA-400 was used as supplied by Sigma-Aldrich. ¹H, ¹³C–{¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance 400 Ultrashield or Bruker Avance 300 Ultrashield spectrometer at 298 K using the residual solvent peak as reference (CDCl₃: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD₂Cl₂: δ_H = 5.32 ppm, δ_C = 54.00 ppm). Peaks are assigned as: s (singlet), d (doublet), t (triplet), h (septet), dd (doublet of doublets), td (triplet of doublets) and m (multiplet). Elemental analyses were performed at Université de Namur, rue de Bruxelles, 55 B-5000 Namur, Belgium.

Experimental procedures

General procedure for the synthesis of IBiox–HCl salts. A 20 mL scintillation vial equipped with a septum cap and a stirring bar was charged with IBiox–HOTf, amberlite (10 mass eq.) in MeOH (0.07 M). The reaction mixture was stirred at room temperature for 2 h. The mixture was filtered through the frit, then washed with DCM (3 times). Evaporation of the solvent, washing with pentane (3 × 3 mL) or recrystallization in the following mixtures of solvents DCM/pentane or in MeOH/Et₂O, followed with drying under high vacuum afforded the products as powders.



Synthesis of (3*S*,7*S*)-3,7-diisopropyl-2,3,7,8-tetrahydroimidazo[4,3-*b*:5,1-*b'*]bis(oxazole)-4-ium chloride (IBiox^tPr-HCl) (2a). Complex 2a was synthesized according to general procedure from IBiox^tPr-HOTf (0.42 mmol, 0.161 g), amberlite (10 mass eq., 1.6 g) in 5 ml of MeOH. Recrystallization in MeOH/Et₂O. White powder, 94.4 mg (83%).

¹H NMR (300 MHz, chloroform-*d*) δ 10.39 (s, 1H, CH), 5.09–4.91 (m, 4H), 4.88–4.79 (m, 2H), 2.62–2.47 (m, 2H, CH-CH₃), 1.08 (d, *J* = 6.9 Hz, 6H, CH₃), 1.00 (d, *J* = 6.9 Hz, 6H, CH₃).

¹³C NMR (75 MHz, chloroform-*d*) δ 125.5 (C–O), 118.6 (CH), 78.9 (O–CH₂), 64.1(CH₂–CH), 31.2 (CH–CH₃), 18.2 (CH₃), 16.8 (CH₃).

HRMS (ESI-TOF): calcd for C₁₃H₂₁ClN₂O₂⁺ [M]⁺: 237.1603; found: 237.1588.

Synthesis of (3*S*,7*S*)-3,7-di-*tert*-butyl-2,3,7,8-tetrahydroimidazo[4,3-*b*:5,1-*b'*]bis(oxazole)-4-ium chloride (IBiox^tBu-HCl) (2b). Complex 2b was synthesized according to general procedure from IBiox^tBu-HOTf (0.51 mmol, 0.209 g), amberlite (10 mass eq., 2 g) in 6.4 ml of MeOH. Recrystallization in DCM/pentane. White powder, 136.6 mg (89%).

¹H NMR (400 MHz, chloroform-*d*) δ 9.75 (s, 1H, CH), 5.10–4.98 (m, 2H), 4.95–4.84 (m, 4H), 1.12 (s, 18H, CH₃).

¹³C NMR (101 MHz, chloroform-*d*) δ 125.7 (C–O), 119.2 (CH), 79.0 (O–CH₂), 68.3 (CH₂–CH), 34.3 (C–(CH₃)₃), 25.8 (CH₃).

HRMS (ESI-TOF): calcd for C₁₅H₂₅ClN₂O₂⁺ [M]⁺: 265.1916; found: 265.1901.

Synthesis of 3,3,7,7-tetramethyl-2,3,7,8-tetrahydroimidazo[4,3-*b*:5,1-*b'*]bis(oxazole)-4-ium chloride (IBioxMe₄-HCl) (2c). Complex 2c was synthesized according to general procedure from IBioxMe₄-HOTf (0.49 mmol, 0.174 g), amberlite (10 mass eq., 1.7 g) in 5.4 ml of MeOH. Recrystallization in DCM/pentane. White powder, 115.6 mg (97%).

¹H NMR (300 MHz, chloroform-*d*) δ 11.06 (s, 1H, CH), 4.64 (s, 4H, CH₂), 1.80 (s, 12H, CH₃).

¹³C NMR (101 MHz, chloroform-*d*) δ 124.5 (C–O), 116.8 (CH), 88.5 (O–CH₂), 64.6 (C–(CH₃)₂), 26.0 (CH₃).

HRMS (ESI-TOF): calcd for C₁₁H₁₇ClN₂O₂⁺ [M]⁺: 209.1290; found: 209.1275.

Synthesis of 2'H,8'H-dispiro[cyclohexane-1,3'-imidazo[4,3-*b*:5,1-*b'*]bis(oxazole)-7',1''-cyclohexan]-4'-ium chloride (IBiox6-HCl) (2d). Complex 2d was synthesized according to general procedure from IBiox6-HOTf (0.44 mmol, 0.192 g), amberlite (10 mass eq., 1.9 g) in 6 ml of MeOH. Recrystallization in DCM/pentane. White powder, 110.7 mg (75%).

¹H NMR (300 MHz, chloroform-*d*) δ 11.18 (s, 1H, CH), 4.77 (s, 4H, O–CH₂), 2.64–2.32 (m, 4H, CH₂), 2.11–1.82 (m, 8H, CH₂), 1.66–1.54 (m, 4H, CH₂), 1.43–1.23 (m, 4H, CH₂).

¹³C NMR (101 MHz, chloroform-*d*) δ 124.1(C–O), 117.3 (CH), 85.8 (O–CH₂), 67.4 (C–CH₃), 35.1(CH₂), 23.7 (CH₂), 23.4 (CH₂).

HRMS (ESI-TOF): calcd for C₁₇H₂₅ClN₂O₂⁺ [M]⁺: 289.1916; found: 289.1903.

General procedure for the synthesis of [Au(IIbiox)Cl] complexes

A 4 mL scintillation vial equipped with a septum cap and a stirring bar was charged with IBiox-HCl (1 eq.), [Au(DMS)Cl] (1 eq.), K₂CO₃ (3 eq.) and acetone (0.5–0.8 mL). The reaction mixture was stirred at 60° C for 1.5–2 h. The solvent was removed under vacuum and purification of the product was carried out by filtration through a millipore membrane filter with DCM (4 mL). Evaporation of the solvent and drying under high vacuum afforded the products as powders.

Synthesis of [Au(IIbiox^tPr)Cl] (3a). Complex 3a was synthesized according to general procedure from IBiox^tPr-HCl (100 mg, 0.367 mmol), [Au(DMS)Cl] (108 mg, 0.367 mmol), K₂CO₃ (152.1 mg, 1.101 mmol) and acetone (0.8 mL), 1.5 h. White powder, 122.1 mg (71%).

¹H NMR (400 MHz, chloroform-*d*) δ 4.91–4.82 (m, 2H), 4.78–4.69 (m, 2H), 4.47–4.36 (m, 2H), 2.89–2.80 (m, 2H, CH-CH₃), 1.02 (d, *J* = 7.0 Hz, 6H, CH₃), 0.87 (d, *J* = 6.8 Hz, 6H, CH₃).

¹³C NMR (101 MHz, chloroform-*d*) δ 124.9 (C–Au), 76.5, 62.2, 30.8 (CH–CH₃), 18.8 (CH₃), 14.9 (CH₃).

Elemental analysis calcd (%) for C₁₃H₂₀AuClN₂O₂: C, 33.31; H, 4.30; N, 5.98; found: C, 33.41; H, 4.49; N, 5.94.

Synthesis of [Au(IIbiox^tBu)Cl] (3b). Complex 3b was synthesized according to general procedure from IBiox^tBu-HCl (50 mg, 0.166 mmol), [Au(DMS)Cl] (49 mg, 0.166 mmol), K₂CO₃ (69 mg, 0.498 mmol) and acetone (0.5 mL), 2 h. White powder, 63.1 mg (76%).

¹H NMR (400 MHz, chloroform-*d*) δ 4.92–4.76 (m, 4H, O–CH₂), 4.20 (dd, *J* = 6.2, 2.2 Hz, 2H, CH₂–CH), 1.18 (s, 18H, CH₃).

¹³C NMR (101 MHz, methylene chloride-*d*₂) δ 151.5, 125.5, 79.1 (O–CH₂), 68.0 (CH₂–CH), 35.4, 27.5 (CH₃).

Elemental analysis calcd (%) for C₁₅H₂₄AuClN₂O₂: C, 36.27; H, 4.87; found: C, 36.29; H, 4.73.

Synthesis of [Au(IIbioxMe₄)Cl] (3c). Complex 3c was synthesized according to general procedure from IBioxMe₄-HCl (50 mg, 0.204 mmol), [Au(DMS)Cl] (60.2 mg, 0.204 mmol), K₂CO₃ (84.7 mg, 0.613 mmol) and acetone (0.5 mL), 1 h. White powder, 63.8 mg (71%).

¹H NMR (300 MHz, chloroform-*d*) δ 4.55 (s, 4H, O–CH₂), 1.75 (s, 12H, CH₃).

¹³C NMR (101 MHz, methylene chloride-*d*₂) δ 143.2, 124.5, 88.4 (O–CH₂), 61.6, 26.5 (CH₃).

Elemental analysis calcd (%) for C₁₁H₁₆AuClN₂O₂: C, 29.98; H, 3.66; N, 6.36; found: C, 29.83; H, 3.69; N, 6.81.

Synthesis of [Au(IIbiox6)Cl] (3d). Complex 3d was synthesized according to general procedure from IBiox6-HCl (50 mg, 0.154 mmol), [Au(DMS)Cl] (45.4 mg, 0.154 mmol), K₂CO₃ (63.9 mg, 0.462 mmol) and acetone (0.5 mL), 1 h. White powder, 54.5 mg (68%).

¹H NMR (400 MHz, chloroform-*d*) δ 4.67 (s, 4H, O–CH₂), 2.59–2.37 (m, 4H), 1.93 (d, *J* = 11.6 Hz, 8H), 1.81–1.64 (m, 2H), 1.46–1.08 (m, 6H).

¹³C NMR (101 MHz, chloroform-*d*) δ 142.4, 123.6, 84.7 (O–CH₂), 35.7 (CH₂), 24.1 (CH₂), 23.7 (CH₂).

Elemental analysis calcd (%) for C₁₇H₂₄AuClN₂O₂: C, 39.21; H, 4.65; N, 5.38; found: C, 39.37; H, 4.55; N, 5.34.



Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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